Airborne, In Situ And Laboratory Measurements Of The Optical And Photochemical Properties Of Surface Marine Waters

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LONG-TERM GOALS

The principal long-term objectives of this work are 1) to uncover and quantify the primary factors controlling the spatial and temporal distributions of the light-absorbing (colored) constituents of dissolved organic matter (CDOM) in marine and estuarine waters, 2) to determine the impact of CDOM on the aquatic light field and remotely-sensed optical signals, 3) to examine the effects of photooxidation on the optical absorption and emission properties of this material, as well as the relationship between the loss of absorption (and fluorescence) by photooxidation and the yield of photochemical intermediates and products. A combination of field and laboratory measurements are being employed to estimate the wavelength dependence of the rates of the photobleaching response and its relationship to organic carbon photooxidation and the production of photochemical intermediates in order to better understand the impact of photooxidation on marine carbon and trace element cycles and the optical properties of seawater.

OBJECTIVES

Our principal near-term objective was to complete one final 5-day research cruise in October 1999 to the Middle Atlantic Bight and the Chesapeake and Delaware Bays. This cruise represented the culmination of a series of ten cruises covering the years from 1993 to 1999. These cruises have examined 1) the seasonal and spatial variability of CDOM absorption and emission in the Middle Atlantic Bight and more recently, in the Delaware and Chesapeake Bays, 2) the contribution of CDOM absorption to the aquatic light field in these regimes, and 3) the effects of stratification on the photodegradation of CDOM and on the vertical structure of the optical properties. Another near-term objective was to develop a model for the photobleaching of CDOM absorption and fluorescence based on an extensive laboratory study of CDOM photobleaching kinetics that employed both monochromatic and broad band light sources (Del Vecchio and Blough, in revision).

APPROACH

One five-day cruise in October 1999 was performed to examine the optical and photochemical properties of waters in the Middle Atlantic Bight and in the Delaware and Chesapeake Bays. Data obtained from these cruises included: 1) optical absorption spectra of CDOM using standard spectrophotometers, 2) continuous onboard fluorescence measurements of CDOM; 3) for selected stations, 3-D fluorescence spectra of CDOM; 4) particle absorption spectra using the filter pad method;

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5) detrital absorption spectra using the methanol extraction method; 6) DOC concentrations; 7) in-water downwelling irradiance and upwelling radiance using a Biospherical Instruments MER (September cruise; L. Harding), 8) above-water irradiance and just below-surface upwelling radiance using the Satlantic surface reference (Ajit Subramaniam); 9) backscattering coefficients employing a Hydroscat 6 backscatter meter and absorption measurements using a Wetlabs AC-9 (Ajit Subramaniam); 10) continuous surface chlorophyll fluorescence measurements; 11) pigments and chlorophyll measurements at selected stations (L. Harding); 12) sampling for laboratory photobleaching and photochemistry experiments.

Our approach for developing a model for photobleaching was to first fit the absorption losses produced by monochromatic irradiation at a series of wavelengths to a single exponential decay (as a first-approximation), both at the irradiation wavelength and at wavelengths not irradiated. Cross-sections for photobleaching (Φ) were then obtained from the expression,

$$\Phi = k(\lambda)/E \qquad 1)$$

where $k(\lambda)$ (s^{-1}) is the first-order rate constant for the loss of absorption obtained from the fit at each wavelength and E is the irradiance (photons cm^{-2} s^{-1}) at the irradiation wavelength. Φ thus represents a matrix of photobleaching cross-sections, with the diagonal elements corresponding to the the cross-sections obtained at the irradiation wavelengths and the off-diagonal elements corresponding to the cross-sections at wavelengths not receiving irradiation. Multiplication of Φ by a vector of irradiances $[E(\lambda)]$, representing the broad-band light field, then provides a vector of first-order rate coefficients $[k(\lambda)]$ that can be used to calculate the photobleaching kinetics (Fig. 1).

To test the model, Φ, generated from a series of monochromatic irradiations of Suwanee River Fulvic Acid (SRFA), was multiplied by the $E(\lambda)$ obtained for a series of different broad-band sources, and the results of the model were directly compared to the wavelength-dependence of the photobleaching response observed in the broad-band irradiations of SRFA (see below).

WORK COMPLETED

1. Over the last year, one additional set of in situ optical and (photo)chemical data, and another set of airborne optical data were acquired for the Middle Atlantic Bight. The PI and his collaborators are currently processing and integrating these data in preparation for publication. Some preliminary results are provided below.

2. A relatively simple and easy to implement photobleaching model was developed and tested against actual broad-band photobleaching data (see below).

Figure 1. Explanation of model calculations.

$\Phi_\lambda = k_\lambda / E$ k_λ = first order decay

E = irradiance at the excitation wavelength

Matrix of Φ_λ based on monochromatic data (Q3 = matrix of Φ_λ 10^{20})

λ_{irr}	300	310	320	330	340	350	360	370	380	390	400
Q3 =	0.217	0.104	0.0775	0.0509	0.0414	0.0319	0.0223	0.0128	0.0103	0.0078	0.00535
	0.213	0.11	0.0833	0.0565	0.046	0.0356	0.0251	0.0146	0.0117	0.00864	0.00571
	0.208	0.11	0.0854	0.0608	0.0499	0.0389	0.0278	0.0169	0.0133	0.00975	0.00624
	0.201	0.107	0.0848	0.0625	0.0518	0.0411	0.0304	0.0196	0.0154	0.0112	0.00709
	0.193	0.103	0.0823	0.0616	0.0517	0.0419	0.032	0.0221	0.0185	0.0149	0.0113
	0.183	0.0972	0.0776	0.058	0.0495	0.0411	0.0326	0.0242	0.0201	0.0159	0.0119
	0.175	0.0924	0.0734	0.0543	0.047	0.0398	0.0326	0.0253	0.0216	0.0179	0.0143
	0.169	0.0891	0.0697	0.0502	0.044	0.0378	0.0315	0.0253	0.0225	0.0198	0.0171
	0.169	0.0864	0.0665	0.0466	0.041	0.0354	0.0279	0.0241	0.0227	0.0213	0.02
	0.166	0.0848	0.0642	0.0435	0.0383	0.0332	0.0281	0.0229	0.0244	0.0258	0.0273
	0.165	0.0804	0.0606	0.0408	0.0359	0.0311	0.0262	0.0213	0.0241	0.0268	0.0296

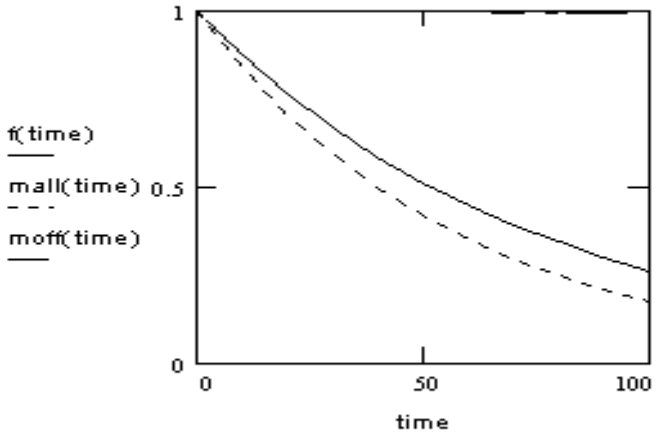
To predict broad band:

(Matrix of Φ_λ)* (Light intensity (E_λ)) = k_λ

[Φ_λ] * [E_λ] = [k_λ]

$$A = A_0 * e^{-k_\lambda t}$$

$$K = \begin{bmatrix} 4.81028 \cdot 10^{-6} \\ 5.34266 \cdot 10^{-6} \\ 5.83978 \cdot 10^{-6} \\ 6.2628 \cdot 10^{-6} \\ 6.77571 \cdot 10^{-6} \\ 6.81867 \cdot 10^{-6} \\ 6.90357 \cdot 10^{-6} \\ 6.88776 \cdot 10^{-6} \\ 6.73349 \cdot 10^{-6} \\ 7.04422 \cdot 10^{-6} \\ 6.89452 \cdot 10^{-6} \end{bmatrix}$$



RESULTS

Although much of the data from the newer field work is still being processed, a preliminary analysis supports the conclusions reached in earlier field studies (Degrandpre, 1996; Vodacek et al., 1995, 1997); in particular, by mid- to late summer, photobleaching can significantly reduce light absorption by CDOM in the surface waters of the shelf (Fig. 2).Thus, stratification of the water column during the summer months appears to "trap" CDOM in a shallow mixed layer where it undergoes substantial photobleaching, whereas the CDOM in the deeper waters below the thermocline is protected due to the limited penetration of UV radiation.

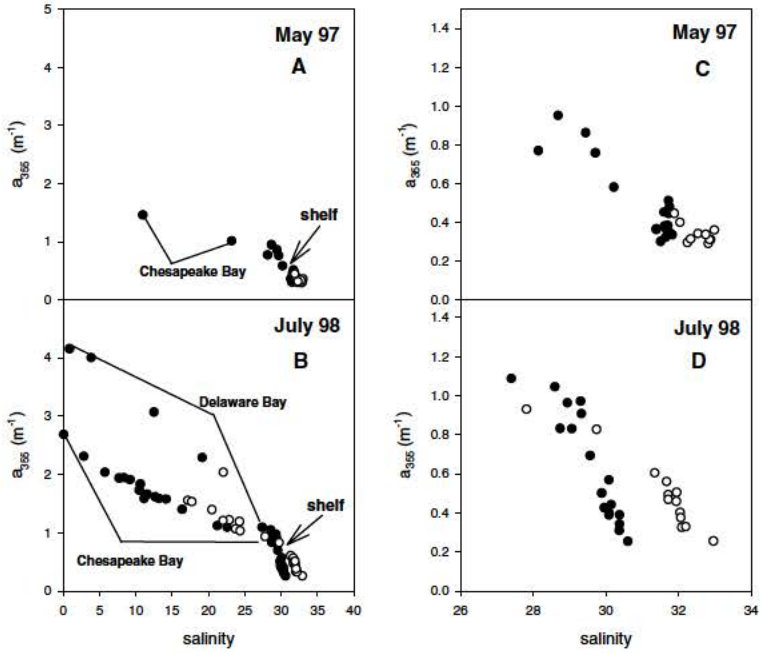


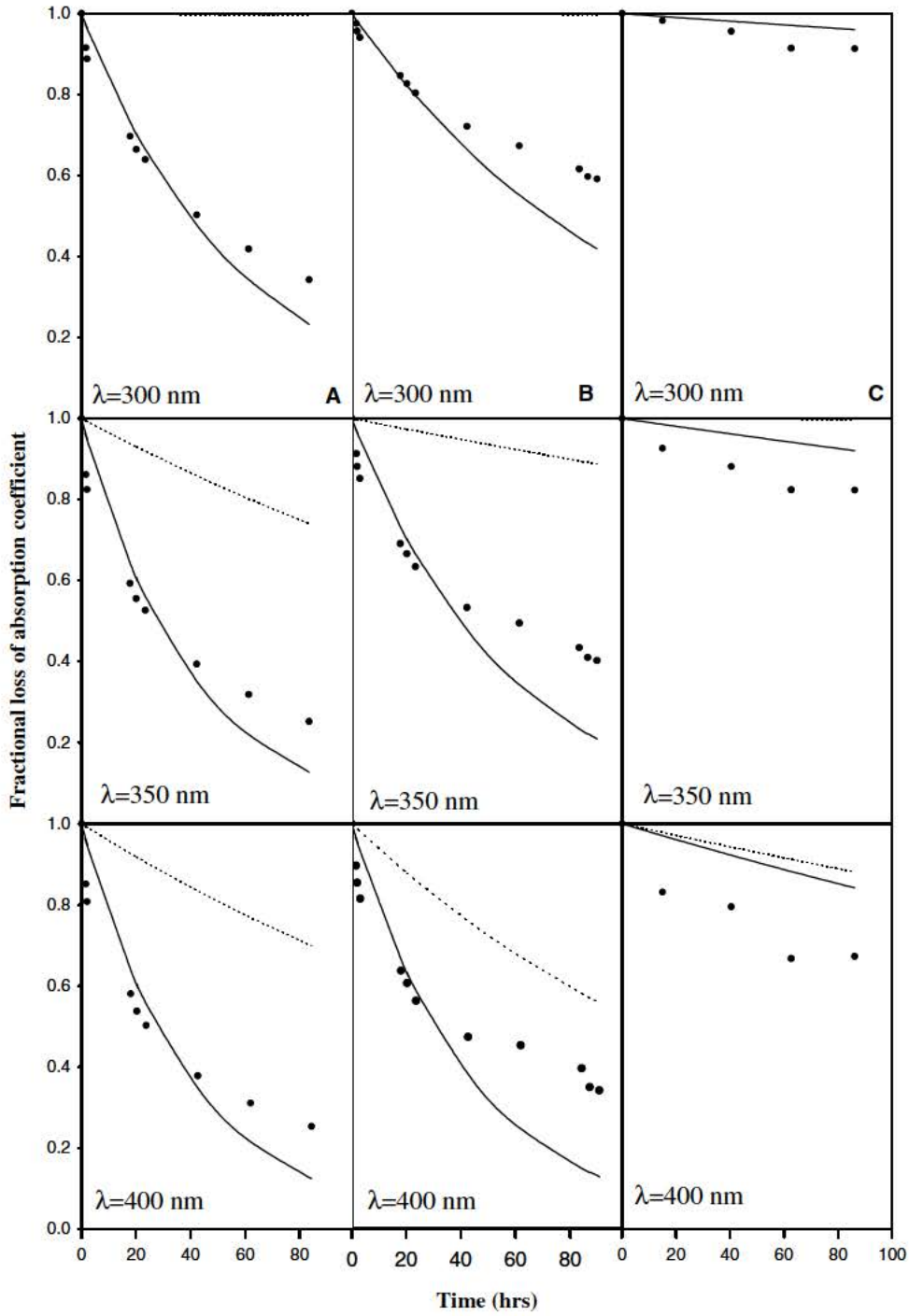
Figure 2. Seasonal variation of the absorption coefficient (a355) versus salinity from the Delaware (and the Chesapeake) Bay to the shelf break. Closed symbols refer to surface waters. Open symbols refer to waters below the mixed layer.

The results obtained in summer can be contrasted with those obtained in late spring (29 May - 4 June 1997; Fig. 2A,C). Although stratification of the water-column was evident, the CDOM absorption coefficients of the surface and deep waters fell on the nearly same mixing line. The absence of a easily discernible photobleaching signal in late (and early) spring is likely due to a number a factors including: 1) mixed-layer depths greater than the UV penetration depth, thus causing the photobleaching signal to be averaged over a greater water-column depth; 2) lower total UV photon dose; 3) the slow kinetics of the photobleaching response.

The ability to predict the photobleaching response under broad-band irradiation conditions using a matrix of photobleaching cross-sections developed for Suwannee River Fulvic Acid is shown in Figure 3. Reasonably good agreement is obtained for the time response of the absorption losses under all of the broad-band light fields examined. The absorption loss with time is significantly

underestimated when the off-diagonal elements are set to zero, clearly illustrating that the absorption losses at wavelengths not receiving irradiation are important to the total absorption loss.

Figure 3. Model of the loss of absorption coefficient under light field >320 nm (column A), >360 nm (column B) and >400 nm (column C). Experimental data, (•); modeled data (—); assumes that only the diagonal elements of matrix are non-zero (···).



IMPACT/APPLICATIONS

The photobleaching model should prove highly useful for predicting the wavelength dependence of the CDOM absorption loss due to photobleaching under most natural settings.

TRANSITIONS

Much of the optical data collected over the last three years on these cruises is being supplied to NASA through Dr. Larry Harding.

RELATED PROJECTS

Over the past year, we have continued our collaborations with Dr. Larry Harding (University of Maryland) and with Dr. Frank Hoge (NASA/Wallops). These collaborations have brought additional expertise and field measurement capabilities to bear on the goals of determining the levels of CDOM and photochemical fluxes remotely via airborne and satellite platforms. During the October 1999 cruise, backscattering coefficients and absorptions measurments were also acquired with a HOBI Labs Hydroscat 6 backscatter meter and WetLabs AC-9, respectively, in collaboration with Dr. Ajit Subramaniam.

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